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Additive influence on Cu nanotube electrodeposition in anodised aluminium oxide templates.

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Abstract

Anodised aluminium oxide (AAO) templates have been utilised to investigate Cu deposition from a typical sulphate plating bath. The influence of the common additives poly ethylene glycol (PEG), chloride ion (Cl^-) and Bis-(sodium sulphopropyl)-disulphide (SPS) on the deposition process has been analysed. The growth of Cu wires or nanotubes (with tube walls of 40-70 nm) is significantly influenced by the action of the additives. In the presence of either Cl^- or SPS solid wire growth is observed, however, when PEG is added with Cl^- the growth of ordered Cu nanotubes is observed. SPS added to a bath containing Cl^- and PEG restores the growth of wires.

Keywords: Templates; AAO; Copper; Electrodeposition; Nanotubes; Additives

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1. Introduction

Metal nanotubes and nanowires are readily fabricated by electrochemical deposition in porous templates [1-5]. Templated electrodeposition has been investigated for a wide variety of applications such as high surface area fuel cell catalysts [6, 7] or battery electrodes [8, 9] where the nanoscale materials exhibit increased functionality by comparison with bulk materials. The formation of either nanotubes or nanowires is typically controlled by the current density utilised [10] which can be exaggerated by the use of low efficiency baths leading to gas evolution during deposition which assists in the formation of nanotubes [11]. Other methods reported to achieve nanotube growth have been pore wall modification to encourage tubular deposition [1], a rotating electric field [12] or the combined effect of the seed layer that extends slightly into the pore and gas evolution [13].

As a potential support material for active outer layers Cu is attractive based on its electrical properties, deposition rate and cost. It has also been extensively investigated for nanoscale deposition of interconnect in the electronics industry. Polyethylene glycol (PEG) and chloride ion (Cl^-) are additives that have been typically used in copper sulphate baths for many years whether for printed circuit board applications [14] or the most advanced sub-100 nm interconnect of Si chips [15-19]. The synergistic effect of these additives and others such as Bis-(sodium sulphopropyl)-disulphide (SPS) required for specific purposes such as enhanced bottom-up fill of blanket seed layer deposited

interconnect vias or trenches have been investigated to enhance the minimum feature size achievable with electrochemical deposition. In this work we analysed Cu deposition from the base of a template which differs from damascene plating in that the side walls of the template are not conductive. We describe the influence of the additives on Cu deposition in porous anodic template materials as a simplified route to the tailored growth of wires or tubes.

2. Experimental

Cu wires and nanotubes were electrodeposited in commercial anodised aluminium oxide (AAO) Anodisc® membranes (Whatman 21 mm diameter exposed, 60 μm thick and 10^9 pores cm^{-2}). The pore diameter was 200 nm. A conductive Ag seed layer 300 nm or 1 μm was deposited on the AAO template by e-beam evaporation (Temescal FC-2000). Electrodeposition was carried out in a 0.24 M $CuSO_4$ (Fisher Scientific, analytical reagent grade) and 1.8 M H_2SO_4 (Air Products, 96%) bath at room temperature with moderate stirring. The additives investigated included poly ethylene glycol (PEG) (300 ppm) (SigmaUltra, mol. wt. 3350, powder) and Cl^- (50 ppm) as NaCl (BDH, analytical reagent grade) and Bis-(sodium sulphopropyl)-disulphide, SPS (Raschig GmbH, Germany) (20 ppm). Cyclic voltammetry was performed using a CH Instruments model CHI 660B potentiostat with a glassy carbon disc working electrode (3 mm diameter, CH Instruments, Inc), Cu foil counter electrode and $Hg/HgSO_4$ reference electrode. The glassy carbon (GC) was polished successively with a 0.3, 0.1 and 0.05 μm alumina powder (Struers) deionised water slurry. Between each stage of polishing, the GC was

cleaned in an ultrasonic bath for 2 minutes to ensure the removal of alumina residues. After sonication, the electrode was rinsed with DI water and dried in a nitrogen flow. Cu electrodeposition in the AAO was performed at 40 mA using the potentiostat in a conventional two-electrode system. The solution volume during copper electrodeposition was 100 ml. The AAO template was mounted vertically in the cell facing the anode with the seed layer on the opposite side open to the solution. The spacing between template and counter electrode was 45 mm. A copper wire was used for electrical connection to the back side (Ag layer) of the template. Electrical contact was made by silver conductive paint left to dry overnight before use. After electrodeposition, the template was removed with 0.75 M NaOH (Sigma-Aldrich, reagent grade, 97%) for 45 minutes. The morphology of electrodeposited Cu nanostructures was analyzed by scanning electron microscopy, SEM (Hitachi S4000).

3. Results and discussion

AAO templates with an evaporated Ag contact layer were utilised to facilitate sub 200 nm Cu electrodeposition. A 300 nm Ag electrical contact layer was deposited on one side of the AAO template. This layer thickness was not sufficient to give a full seed layer coverage of the alumina template. To verify that nanotube growth could be achieved from substrates with a complete seed layer a 1 μm Ag film was also investigated as the seed layer for Cu deposition in the AAO templates. These thicker seed layer deposited films completely covered the pores and led to a solid substrate for the electrodeposition from the outset. Solid wires were observed for the deposition from a typical high efficiency

$CuSO_4$ / H_2SO_4 bath and those with either Cl^- or PEG added, Fig. 1(a). When both Cl^- or PEG additives were in the bath the growth mechanism led to Cu nanotube formation at a lower rate, Fig. 1(b). XRD analysis indicated typical Cu {111}, {200} and {220} peaks for both deposit types and a Ag {220} peak from the seed layer.

The Cu nanotube growth rate was 3.9 nm/s at 40 mA when 300 ppm PEG and 50 ppm Cl^- were present in the bath. This is shown in Fig. 2 for wires and tubes deposited in templates for times ranging from 10 to 60 minutes where the deposit was measured by SEM. The formation of solid wires (at ~ 5.4 nm/s) in baths that did not have both Cl^- and PEG additives and Cu nanotubes when they were both in the bath was seen regardless of whether the evaporated Ag layer was 300 nm or 1 μm. This indicates that the wire or tube growth was independent of whether the base layer was initially intact or developed during deposition. Indeed it was observed that solid wire growth 1-2 μm into the template occurred when building up the backing layer with the front face protected. In all cases where nanotubes were formed the backing electrical contact formed a solid base and whether wire or tube growth was observed depended only on the additives present. Given that the nanotube deposition rate is slightly lower than the wires and the fact that the tube structures represent a significant decrease in Cu content we can estimate an average bath efficiency of 54% for the data in Fig 2 where a tube wall thickness of 50 nm is assumed. Increasing the ratio of PEG (up to 1000 ppm) to Cl^- (50 ppm) led to further decreases in the deposition rate for the nanotubes

The addition of 20 ppm SPS facilitated the reestablishment of solid wire growth from a bath containing Cl^- and PEG which in the absence of SPS gave nanotube growth. It is well known that PEG or Cl^- alone do not influence the Cu deposition process significantly on planar or structured substrates [14-19]. When they are both added however, an inhibition of the Cu deposition process is observed. Surface-enhanced Raman spectroscopy studies indicate that a bridging Cl^- : Cu(I) : PEG complex is formed at the substrate where the Cu(I) is bound to the Cl^- and two oxygen atoms of the PEG chain. [20] The SERS analysis has also indicated that the negatively charged Cl^- gradually desorbs at more negative potentials but that the inhibition of the deposition continues by the action of the uncharged and possibly physisorbed PEG. [14, 20]

The cyclic voltammograms of Fig. 3 show the first cycle deposition and dissolution of Cu at a glassy carbon disc electrode (—) without additives (--) with Cl^- and PEG and (····) with Cl^-, PEG and SPS. Despite initially exhibiting a slightly higher current for Cu deposition at low overpotentials the bath with Cl^- and PEG leads to an inhibition of Cu deposition with less Cu available subsequently for dissolution on the reverse sweep. The deposition peak is clearly shifted by approximately 100 mV in the bath with the Cl^- : PEG. The SPS containing bath also exhibits slightly higher current in the low overpotential region than in the case of the $CuSO_4$ / H_2SO_4 only bath. The SPS is effective in minimising the influence of the Cl^- : PEG adsorbed complex on the Cu deposition and dissolution process. In the templates the accelerator influence of the SPS was also recorded as an increase in the deposition rate (to 7.5 nm/s) for the wire deposits with higher ratios of SPS (up to 200 ppm) in the presence of PEG and Cl^-.

When depositing in the AAO template solid wire growth is observed from the conducting base from simple $CuSO_4$ / H_2SO_4 baths and those containing either Cl^- ion or PEG. When both of these additives are in solution their inhibiting effect is observed and the deposition becomes less efficient at the same current densities. The resulting deposit forms nanotubes with tube walls in the region of 50 nm thickness. The addition of SPS to a bath containing both Cl^- and PEG leads to solid wire growth once more at a fresh substrate. This may be understood in terms of the estimated faster diffusion coefficient of SPS (10^{-5} cm^2/s) by comparison with PEG (5×10^{-7} cm^2/s) [17] The SPS which has diffused faster to the base of the pore prevents the PEG based complex adsorbing and inhibiting the growth thus leading to solid wire growth. At longer times SPS effectively displaces any adsorbed Cl^- : PEG complex and maintains the solid wire Cu deposition.

Fig 4 is a schematic representation of the proposed deposition process. Fig 4 (a) represents a cross section of the base of the AAO with 300 nm Ag seed layer. Fig. 4 (b) represents the early stages of Cu growth with wires forming in the template and the base layer increasing in thickness. Fig. 4 (c) shows the wires formed and the resulting thick base layer that supports the wires and assists with their vertical alignment after the AAO is removed. The removal is achieved in alkaline solution and represented in Fig 4 (d) and in the SEM image of Fig. 1 (a) above. The alternative route c' and d' is taken when the additives Cl^- and PEG are both present in the bath. In that case the inhibitory influence of the adsorbed Cl^- : PEG complex [15-20] leads to an increase in the overpotential for the reaction taking the deposition into the hydrogen region resulting in gas evolution which

promotes tube growth by forcing the reaction to occur at the sides of the porous templates by shielding the central portion of the structure and preventing deposition in that region. [11] This results in a lower deposition rate for an identical deposition current as discussed above. The second effect of the adsorbed Cl^- : PEG complex is on the seed layer where the deposition is inhibited in the central portion of the base or seed layer thereby promoting the deposition around the edge of the seed layer resulting in the formation of nanotubes. The PEG complex which is assumed to be spherical [16, 17] may be sterically impeded at the template wall or the alumina may present energetically favourable sites [10] for metal atom adsorption leading to preferential Cu nucleation and lower overpotential tube growth.

4. Conclusion

The influence of the additives PEG, Cl^- and SPS which are commonly used in Cu plating baths has been shown to result in either wire or tube growth in AAO templates. Tailoring the bath composition can result in either form of the templated structure. This process eliminates the need to develop low efficiency baths that favour hydrogen evolution rather than the metal deposition or more complicated processing such as pretreatment of the template walls or a specific apparatus to rotate electric fields during deposition. The resulting deposits can be utilised as high surface area supports for energy devices or sensor applications. The results also have implications for high aspect ratio Cu deposition where the seed layer is confined to the base of the structure.

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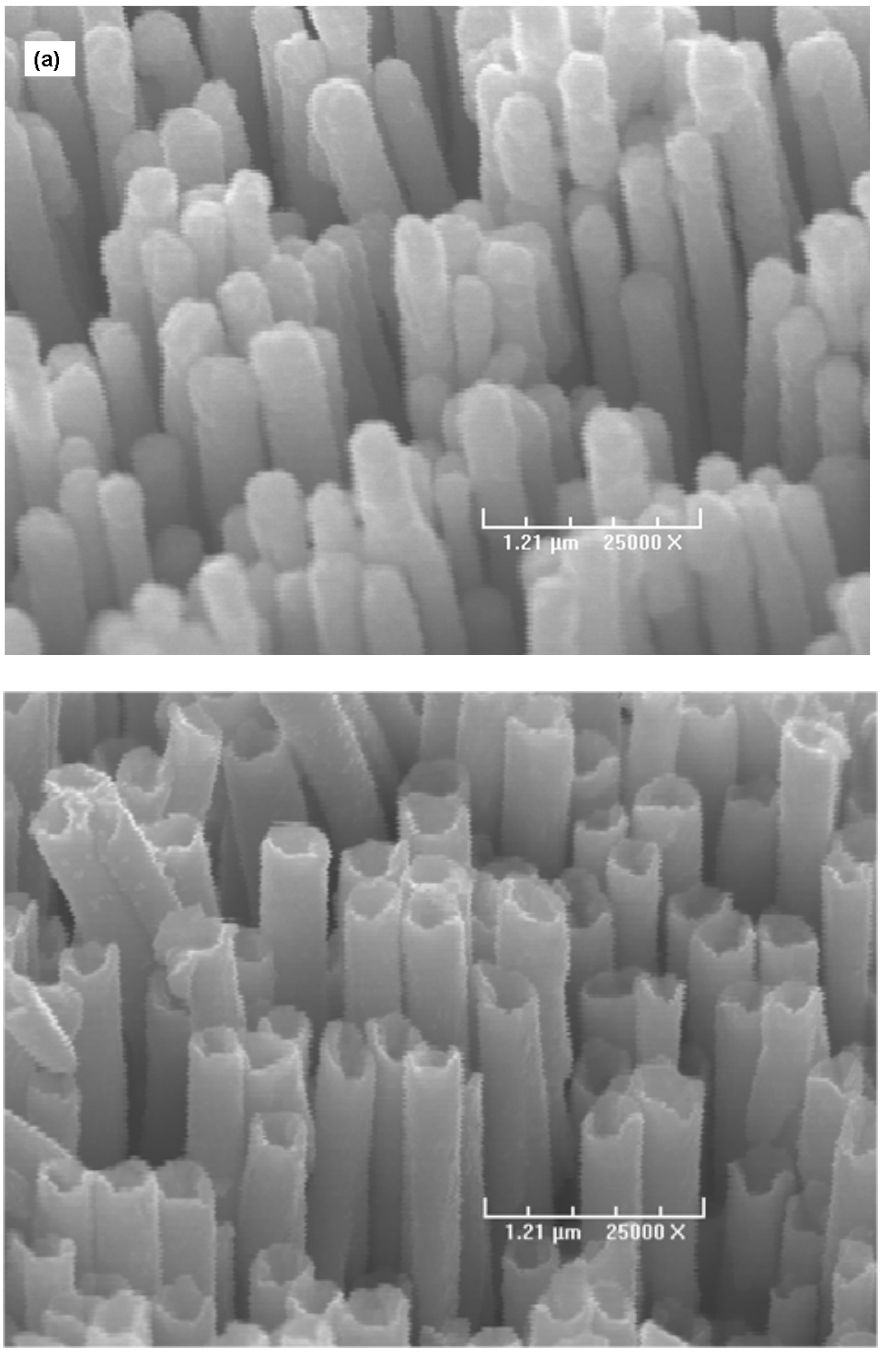


Fig. 1. (a) Array of Cu wires deposited from 0.24 M $CuSO_4$ in 1.8 M H_2SO_4 with 300 ppm PEG added (b) Array of Cu nanotubes deposited from 0.24 M $CuSO_4$ in 1.8 M H_2SO_4 with 50 ppm Cl^- and 300 ppm PEG added following dissolution of the AAO template.

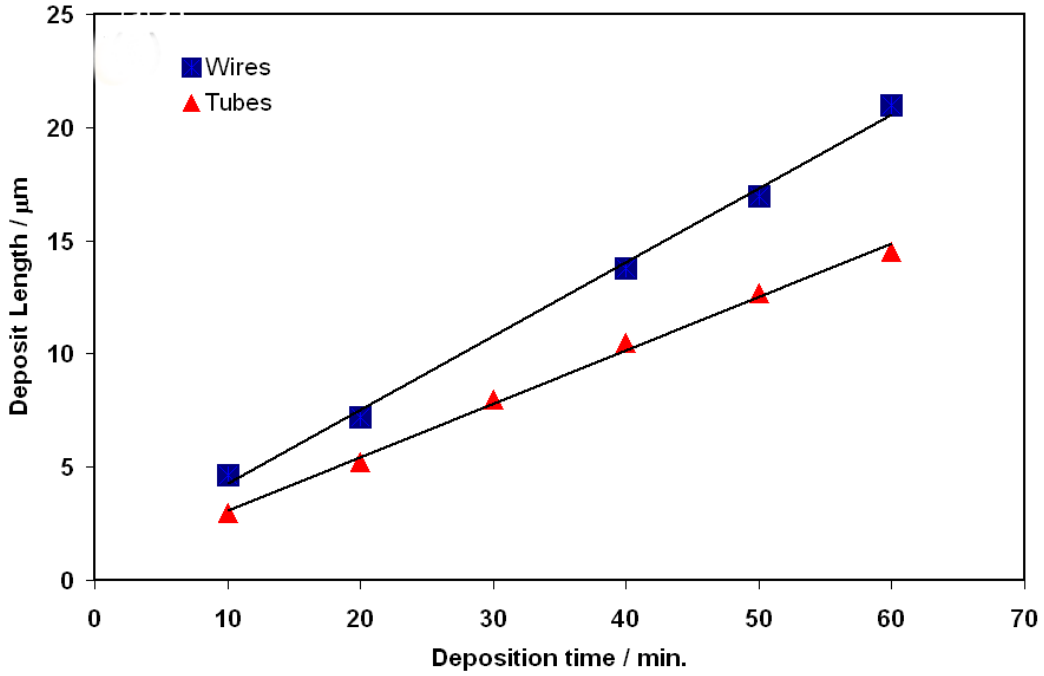


Fig. 2. Deposition rates for the growth of wires in 0.24 M $CuSO_4$ in 1.8 M H_2SO_4 bath and tubes when both 50 ppm Cl^- and 300 ppm PEG are added to the solution.

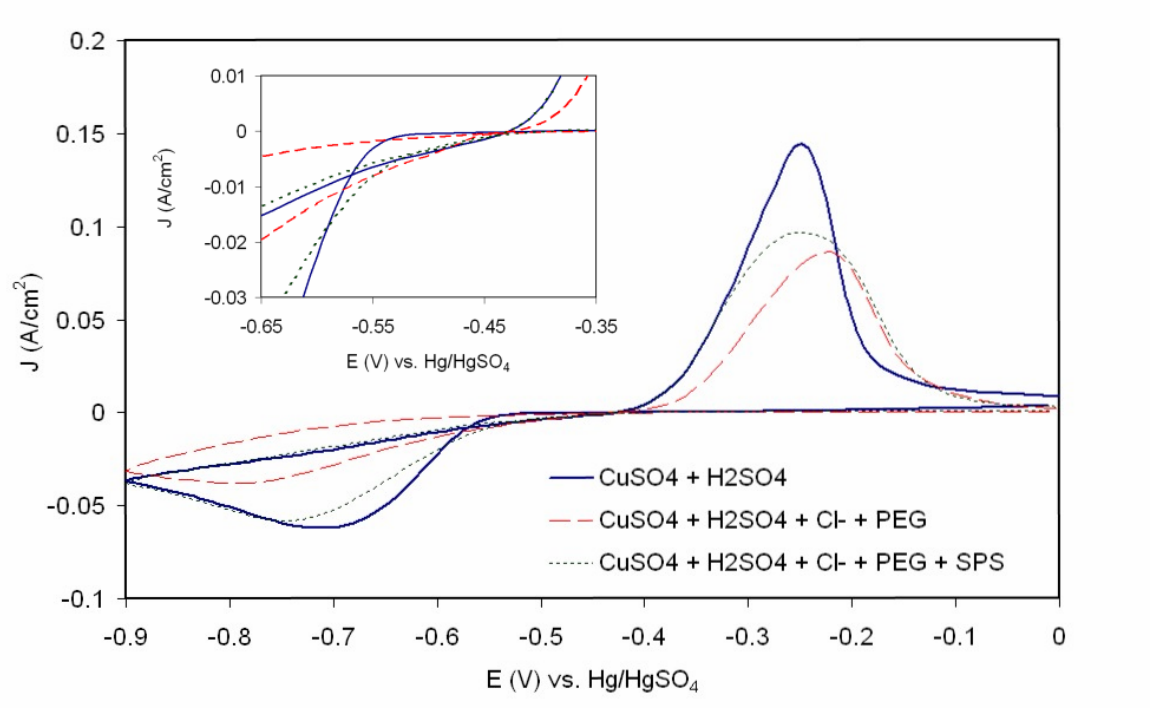


Fig. 3. Cyclic voltammograms (0 V to -0.9 V at 50 mV/s) at a glassy carbon disc electrode and inset enlarged low overpotential region.

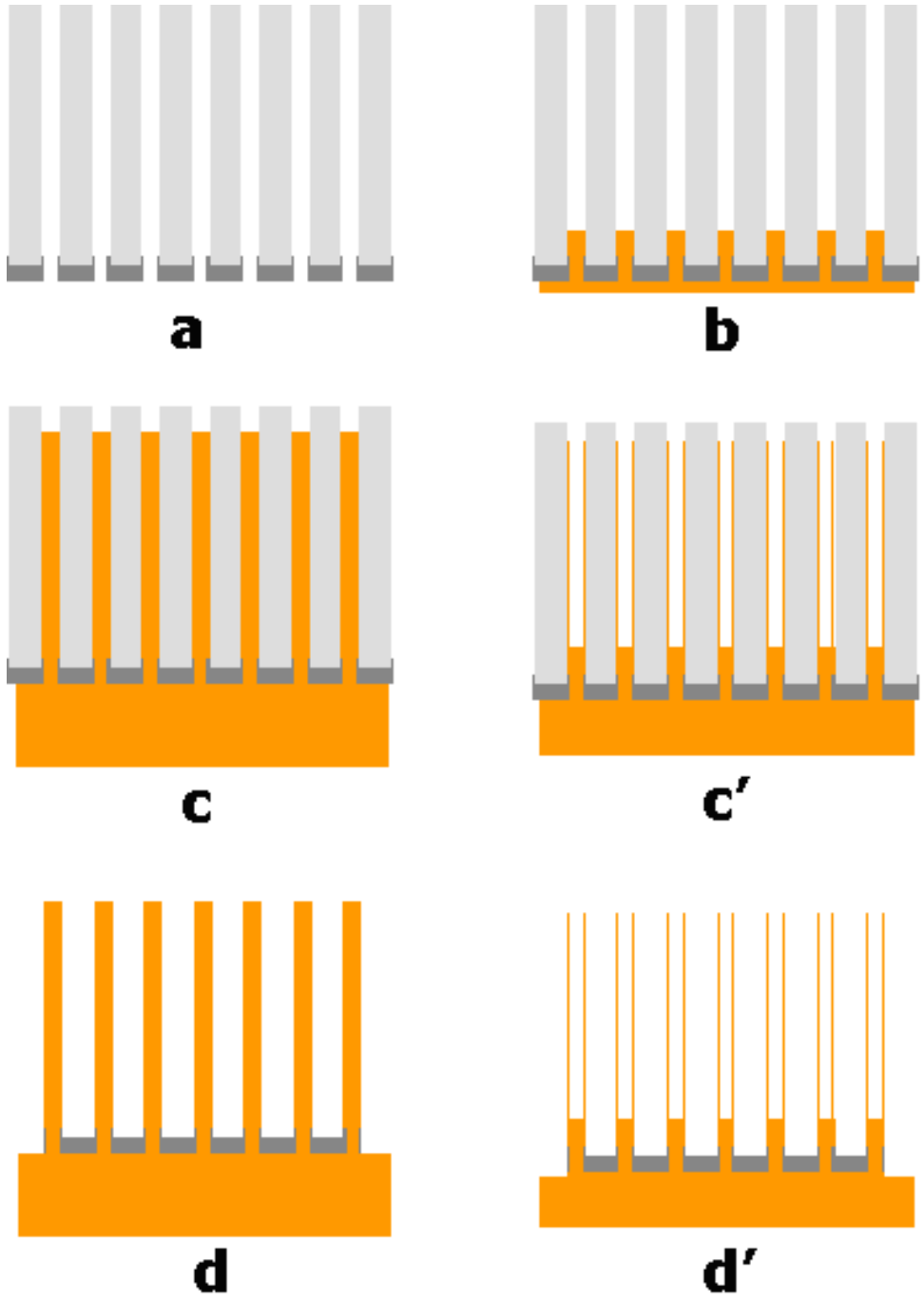


Fig. 4 Schematic of the general process involved in wire or tube electrodeposition dependent upon the additives utilised as described in the text.